

## C/SiC LIFE PREDICTION FOR PROPULSION APPLICATIONS

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### ABSTRACT

Accurate life prediction is critical to successful use of ceramic matrix composites (CMC). The tools to accomplish this are immature and not oriented toward the behavior of carbon fiber reinforced silicon carbide (C/SiC), the primary system of interest for many reusable and single mission launch vehicle propulsion and airframe applications. This paper describes an approach and progress made to satisfy the need to develop an integrated life prediction system that addresses mechanical durability and environmental degradation of C/SiC. Issues such as oxidation, steam and hydrogen effects on material behavior are discussed. Preliminary tests indicate that steam will aggressively remove SiC seal coat and matrix in line with past experience. The kinetics of water vapor reaction with carbon fibers is slow at 600°C, but comparable to air attack at 1200°C. The mitigating effect of steam observed in fiber oxidation studies has also been observed in stress rupture tests. The effects of oxidation on tensile strength after low levels of oxidation in air at intermediate temperatures have been determined. Detailed microscopy of oxidized specimens has been carried out to develop a diffusion and reaction kinetics based oxidation model. Mechanical property tests to develop and verify the probabilistic residual strength have been completed at 1200 and 800°C. Gage width is a key variable governing edge oxidation of seal coated specimens. Future efforts will include architectural effects, enhanced coatings, biaxial tests, and LCF.

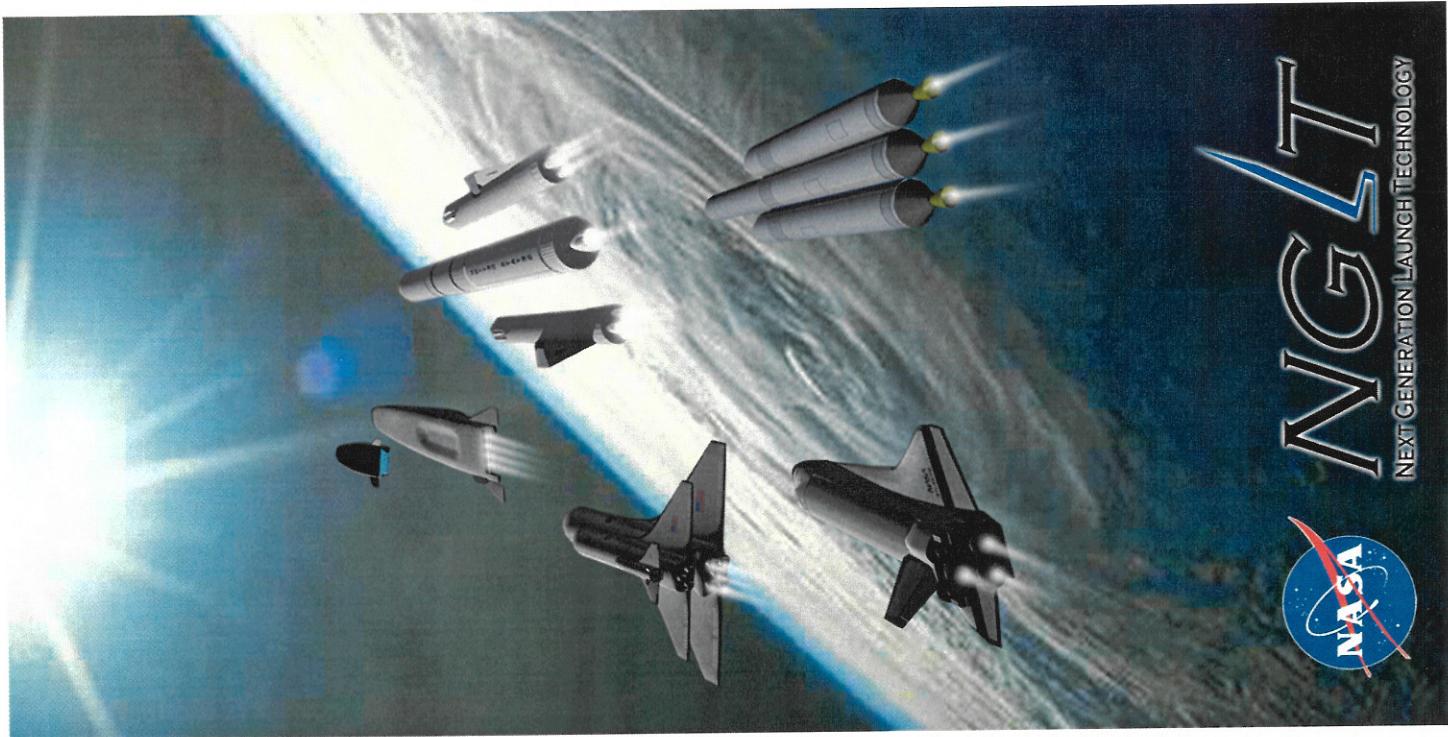
Keywords: ceramics, composites, life prediction, carbon fibers, oxidation, stress rupture

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28th Annual Conference on Composites, Materials and  
Structures  
by the  
Ceramic, Metal and Carbon Composites Committee (CMC<sup>3</sup>)  
of the  
Advanced Composites Working Group (ACWG)  
Cape Canaveral, FL  
January 25-30, 2004.



NGLT

NEXT GENERATION LAUNCH TECHNOLOGY

## OUTLINE

- ◆ Introduction
- ◆ Oxidation Models
  - Effect of environment
  - Gage width
  - Residual strength
- ◆ Steam Effects on SiC Seal Coat and Matrix
- ◆ Concluding Remarks

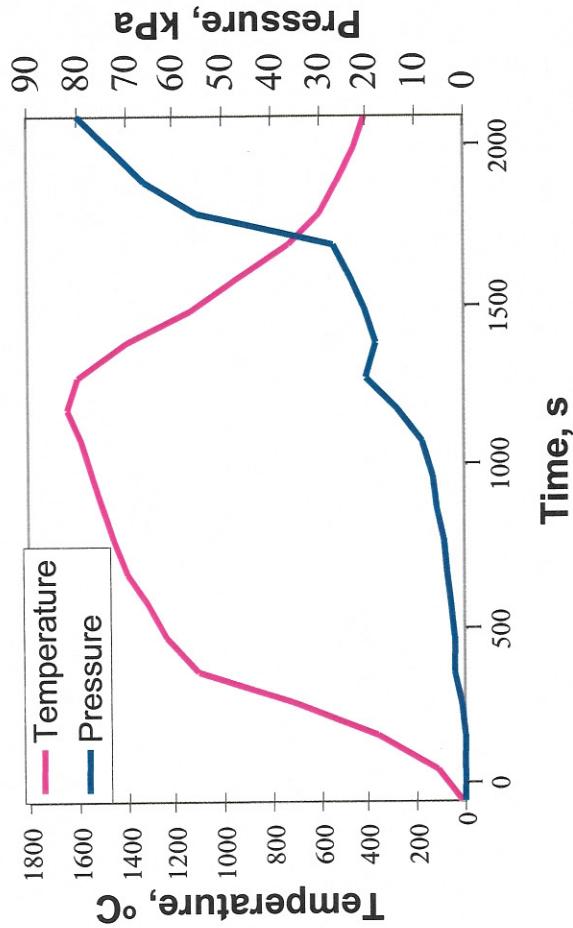
# Demanding Environments Push CMC Materials Limits

## PROPELLION

- ◆ High temperatures (~ 3500R)
  - Low and intermediate temperatures can also be a problem
- ◆ High pressures (e.g. to ~ 6000psi)
- ◆ Severe chemical environments
  - Steam
  - Oxygen rich or fuel rich
  - Hydrogen
  - High velocity
- ◆ Exposure cycles from minutes in rockets to ~ hours in some combined cycle approaches
- ◆ Severe thermal transients and gradients
- ◆ 100 flight reusability

## AIRFRAME

X-38 Reentry Profile for Body Flap Windward Surface Location



# Task Objectives

- ♦ **Primary goal:**
  - Develop and verify a robust methodology for confident determination of the reusable life capability of C/SiC space propulsion hardware.
- ♦ **Secondary goals:**
  - To ground the methodology with mechanism-based descriptions of mechanically and environmentally induced damage.
  - To expand the database for C/SiC.
  - To directly support flight experiments which use CMC propulsion components.

# Materials

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- ♦ Plain weave C/SiC with seal coat
- ♦ Enhanced with seal coat
  - plain weave
  - 5 harness satin weave
  - w/wo CBS coating

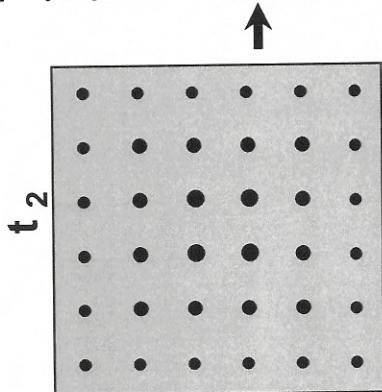
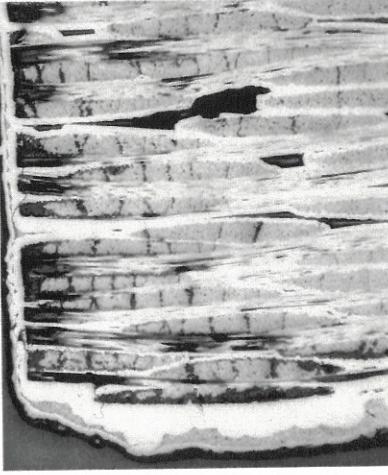
# C/SiC Life Controlled by Complex, Interactive Mechanisms

- ◆ Environmental
  - surface recession due to moisture
  - interface and fiber oxidation
- ◆ Mechanical
  - strains due to thermal and mechanical loads
  - cycling of loads (LCF, HCF)
  - creep

## Temperature Dependent Carbon Fiber Oxidation Mechanism

### Low Temperature Regime

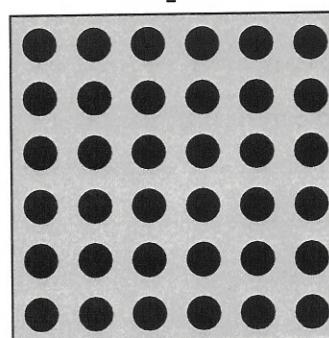
- Controlled by C/O<sub>2</sub> reactions
- Entire section saturated in O<sub>2</sub>
- Similar reactivity throughout



**Reaction  
Controlled**

750°C  
172 MPa  
(25 ksi)

Starting Matrix  
→ 6x6 Fiber Tow  
Array



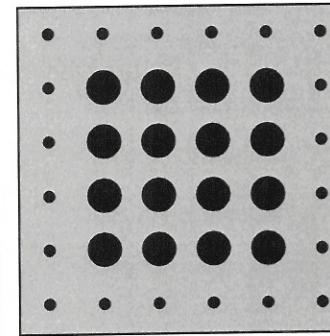
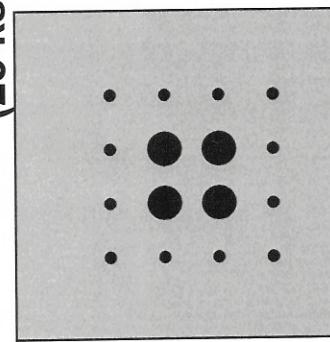
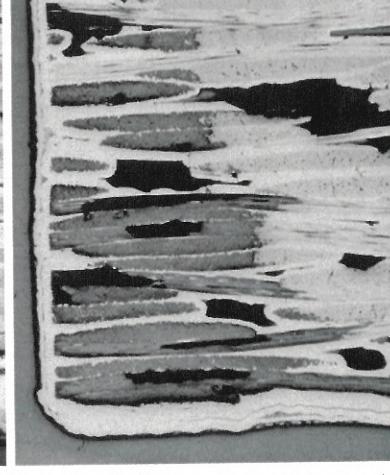
t<sub>0</sub>

t<sub>1</sub>

t<sub>2</sub>

### High Temperature Regime

- Controlled by oxygen supply
- Large gradient in O<sub>2</sub> conc.
- Moving reaction front, shrinking core



**Diffusion  
Controlled**

t<sub>1</sub>  
t<sub>2</sub>

## Linear and Parabolic Oxidation Models

- ◆ Parabolic kinetics, no role of Knudsen diffusion

Composite cross-section



$$x^2 = k_p t = k_p^* t T^{1/2} \ln(1 + \Phi)$$

- ◆ Linear kinetics (Reaction Control)

$$x = k_l t = k_l^* t (\Phi P/T) \exp(-Q/RT)$$

### TWO CASES

- Totally reaction controlled oxidation – uniform attack of each fiber
- Localized attack down cracks leading to fiber flaws and strength degradation

$$\sigma_t = \sigma_o (d_o - k_l t)^2 / d_o^2$$

$$\sigma_t = \sigma_o K / C^{1/2} = \sigma_o K / (k_l t)^{1/2}$$

for  $C > C_o$

$x$  = measure of damage, cm

$T$  = temperature, K

$t$  = time, s

$\Phi$  = oxygen mole fraction

$k_p, k_p^*$  = parabolic rate constants

$k_l, k_l^*$  = linear rate constants

$P$  = total pressure, atm

$R$  = constant, kcal/mole-K

$Q$  = activation energy, kcal/mole

$\sigma_o, \sigma_t$  = initial and degraded strength, MPa

$K$  = constant,  $d_0$  = initial diameter, cm

# Application of Reaction Controlled Life Models

- ◆ Linear kinetics

- ◆ Uniform Attack

$$x = k_l t = k_l^* t (\Phi P/T) \exp(-Q/RT)$$

$$\sigma_t = \sigma_o (d_o - k_l t)^2 / d_o^2 \quad (1)$$

When  $\sigma_t = \sigma_{\text{appl}}$  the composite fails

Substituting for  $\sigma_t$  and  $k_l$  in eq. (1), combining constants and solving for  $t$  gives

$$t = \frac{\mathcal{L} T \exp(Q/RT) \{1 - (\sigma_{\text{appl}}/\sigma_o)^2\}}{\Phi P}$$

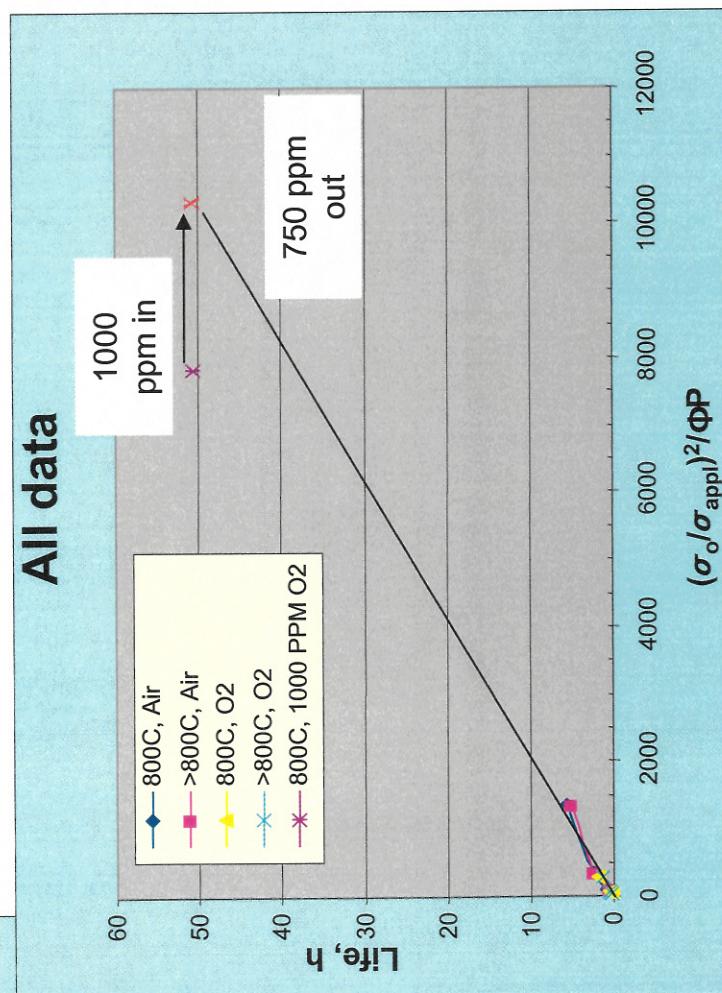
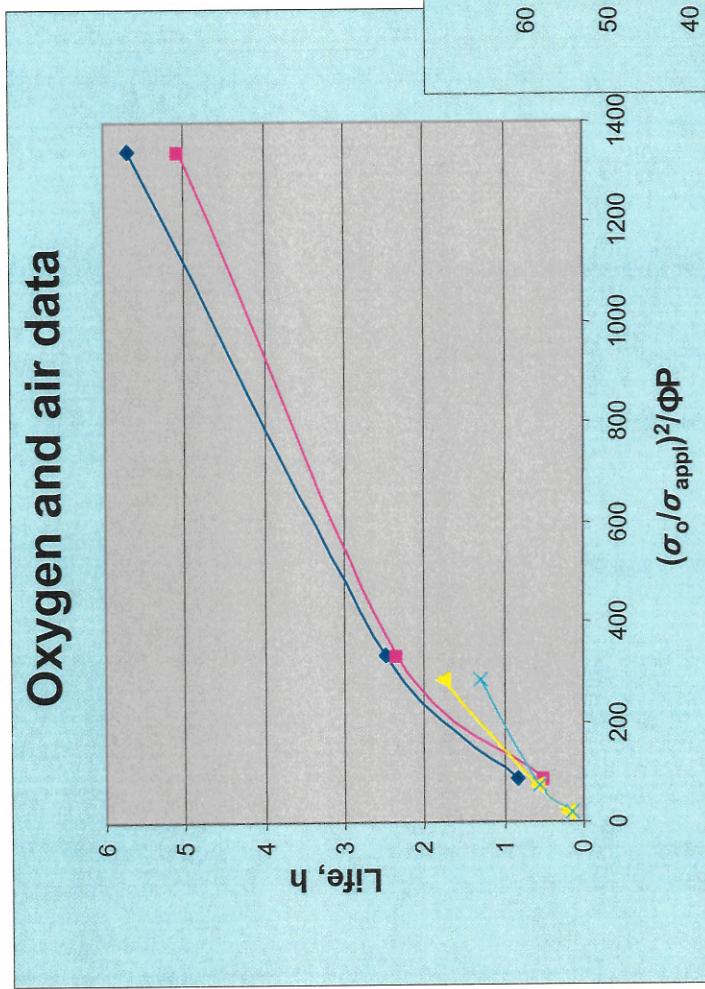
- ◆ Local Attack

$$\sigma_t = \sigma_o K / (k_l t)^{1/2}$$

Substituting for  $\sigma_t$  and  $k_l$ , combining constants and solving for  $t$  gives

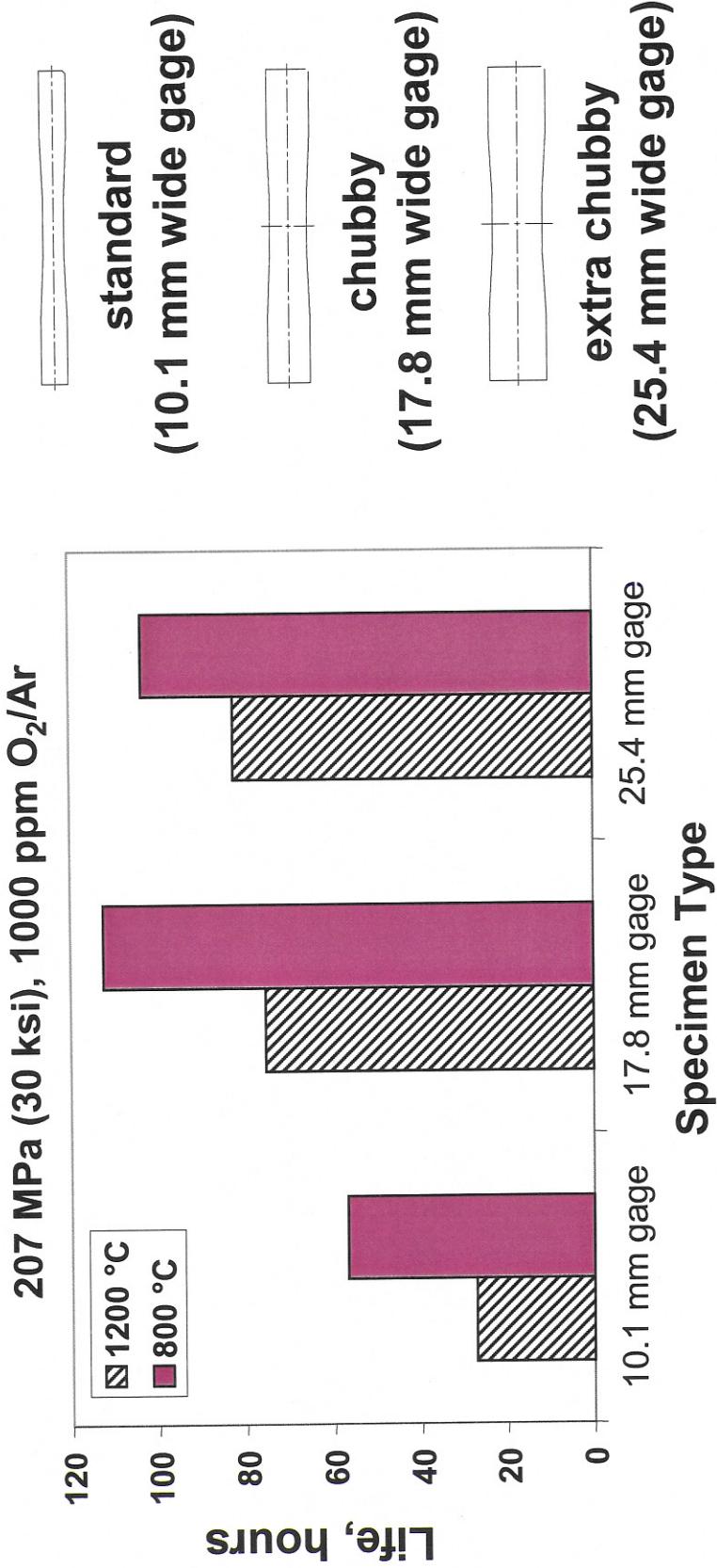
$$t = \frac{\mathcal{L} T \exp(Q/RT) \{\sigma_o / \sigma_{\text{appl}}\}^2}{\Phi P}$$

## Local Fiber Damage Approach for Reaction Control Fits Data Over a Wide Range of Pressure and Stress



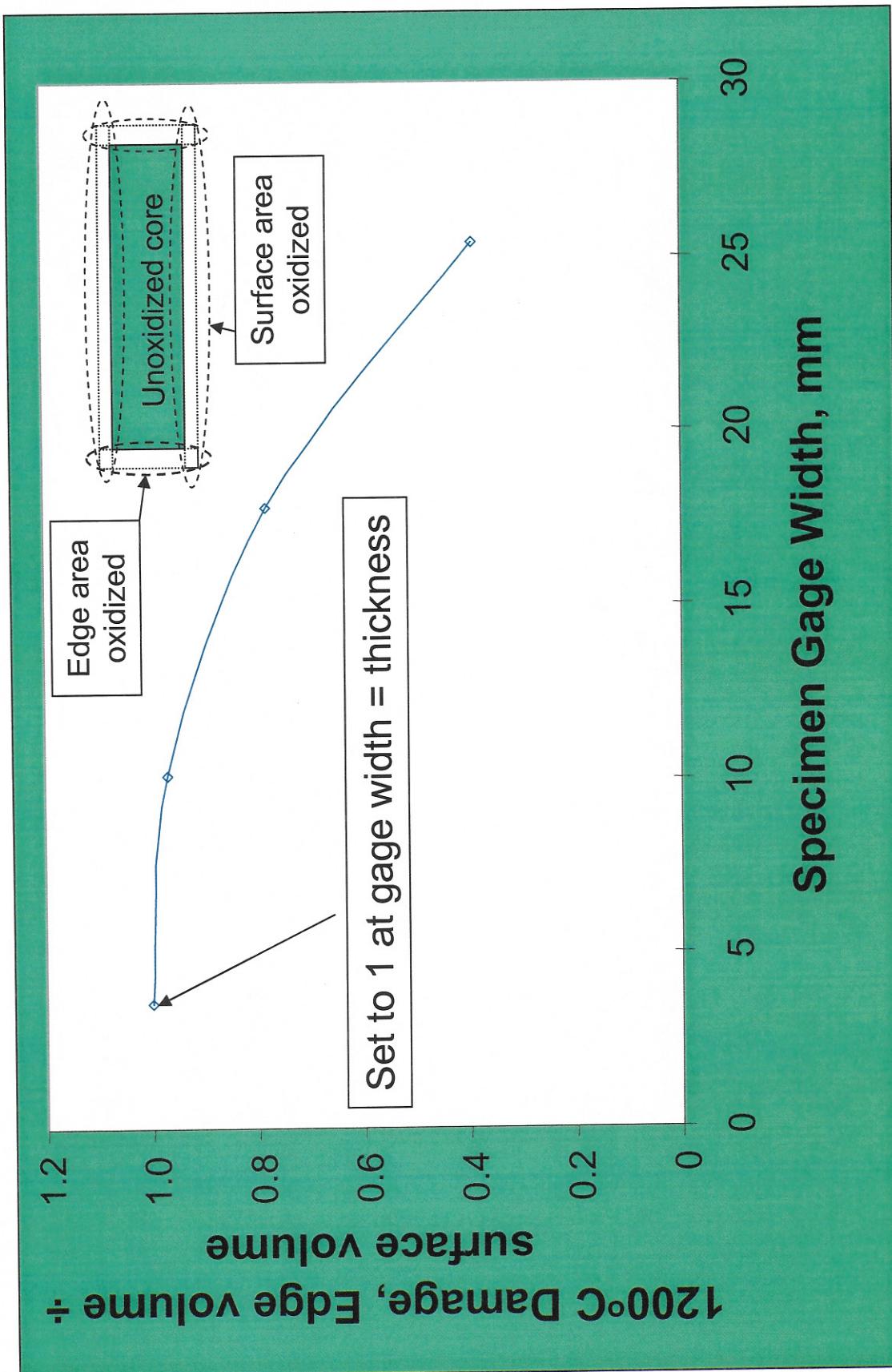
- ◆ Pressure range: 1000 ppm O<sub>2</sub> to 1 atm O<sub>2</sub>
- ◆ Stress range: 35 to 207 MPa
- ◆ Good fit to model = straight line through the origin

## Stress Rupture Life Is a Function of Specimen Width for C/SiC

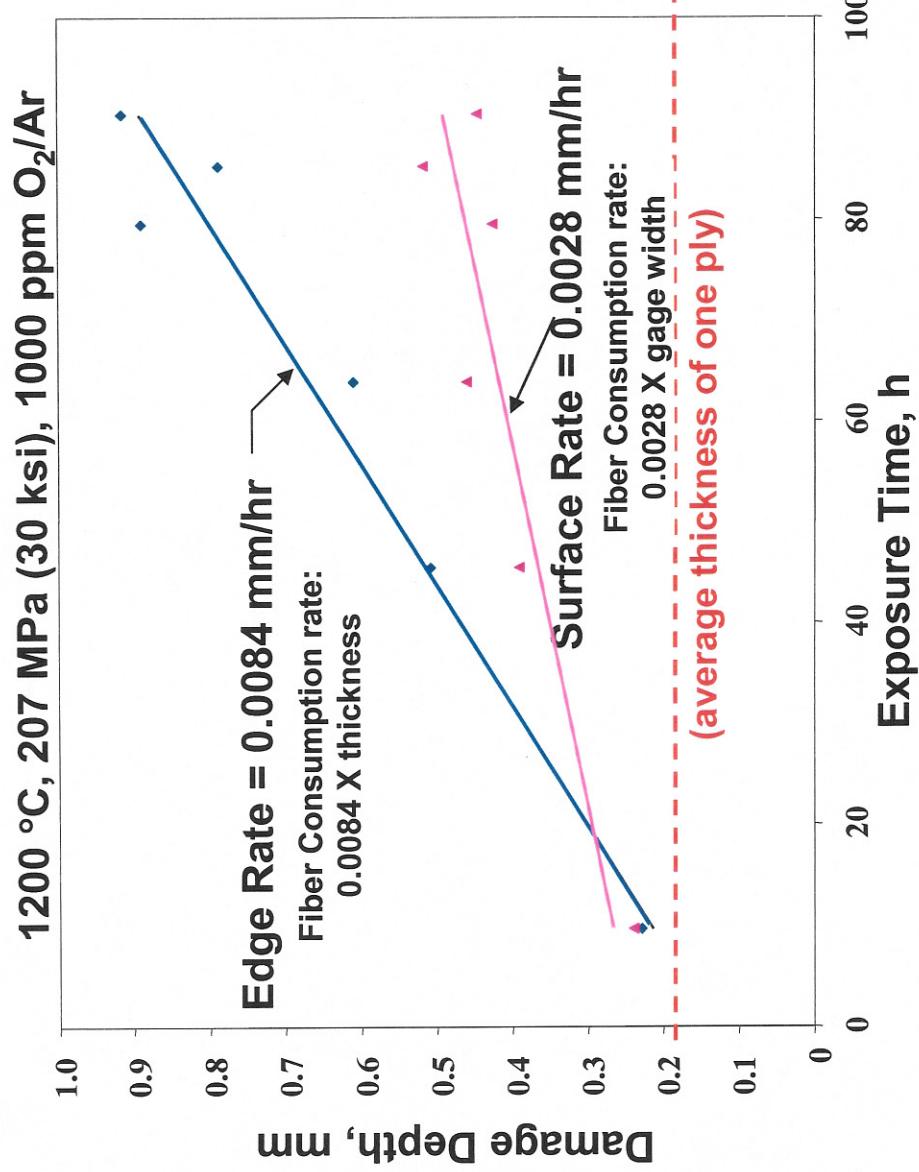


- ◆ Material volume effects need to be incorporated in life prediction models.
- ◆ Average life at 800°C is about 1.5 times longer than at 1200°C.
- ◆ 17.8 mm wide specimens resulted in about a 2.5 increase in life compared to 10.1 mm wide specimens.

# Edge Damage Effects Insignificant for Large Panels



# C/SiC Oxidation Damage Rates



- ◆ Surface damage penetration rate is 1/3 edge penetration rate
- ◆ Highest volume of carbon fiber is consumed by surface penetration

## Application of Parabolic Life Model

- ◆ Assume parabolic kinetics at all temperatures and no role of Knudsen diffusion
- Rationale: 1 atm total pressure with 1000 ppm O<sub>2</sub> eliminates reaction controlled kinetics

$$x^2 = k_p^* t T^{1/2} \ln(1 + \Phi)$$

$$x = (k_p^* t T^{1/2})^{1/2} (\ln(1+\Phi))^{1/2}$$

- ◆ Assume purely case/core mode of fiber attack

$$\text{Initial area} = A_o = w_o h_o$$

$$\text{Residual area} = A_r = w_o h_o - (2w_o + 2nh_o)x \text{ for observed edge attack rate} = n \text{ times surface attack rate}$$

- For applied load P<sub>appl</sub> = σ<sub>appl</sub> w<sub>o</sub> h<sub>o</sub> failure occurs when the stress increases to σ<sub>ult</sub>

$$\sigma_{ult} = \sigma_{appl} w_o h_o / (w_o h_o - (2w_o + 2nh_o)x)$$

$$w_o h_o / (w_o + nh_o) = 2x / (1 - \sigma_{appl} / \sigma_{ult}) = 2 (k_p^* t T^{1/2})^{1/2} (\ln(1+\Phi))^{1/2} / (1 - \sigma_{appl} / \sigma_{ult})$$

Solving for t<sup>1/2</sup>

$$t^{1/2} = \{(1 - \sigma_{appl} / \sigma_{ult}) w_o h_o / (w_o + nh_o)\} / 2 (k_p^* T^{1/2})^{1/2} (\ln(1+\Phi))^{1/2}$$

- For constant environmental conditions, plot

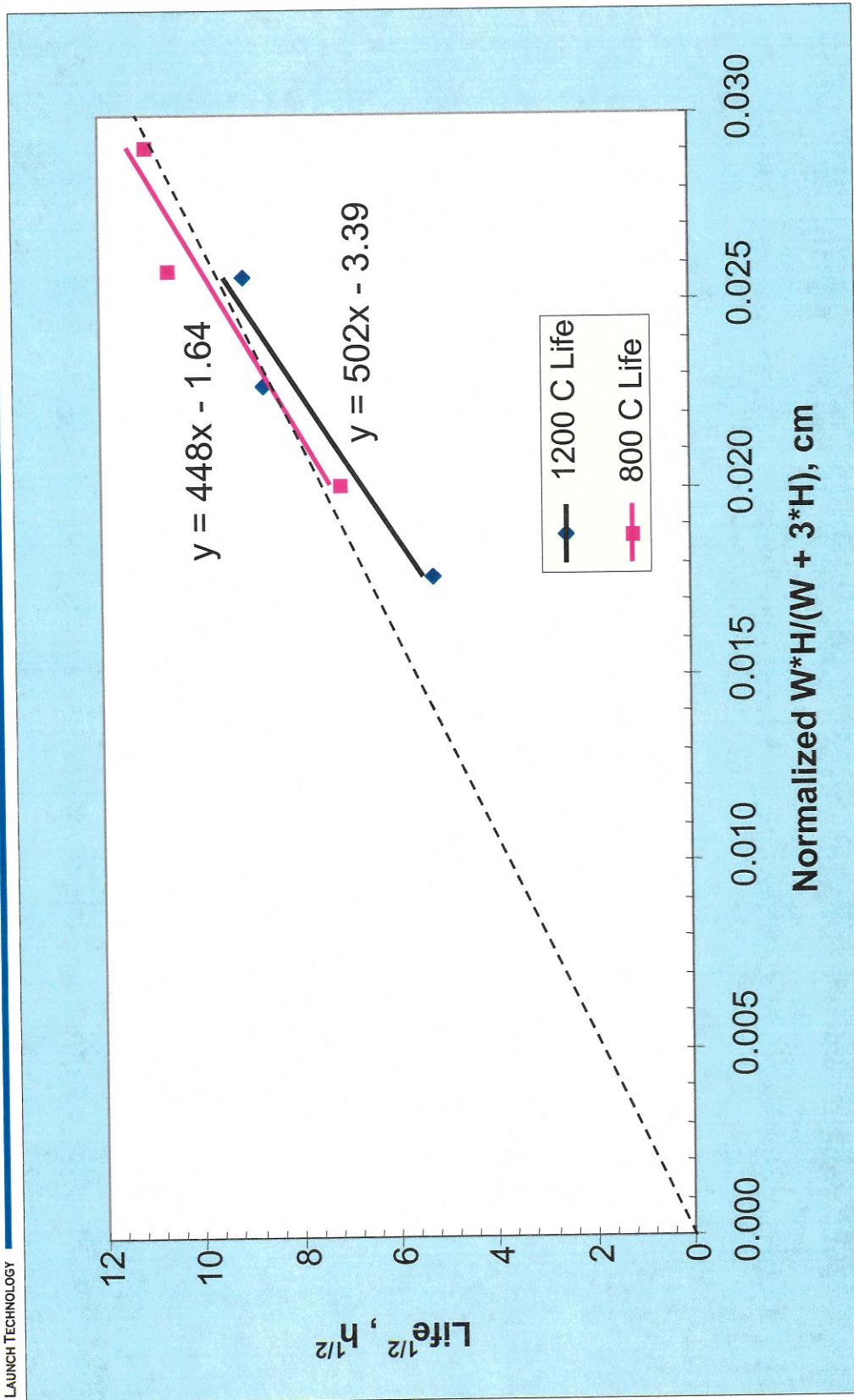
$$t^{1/2} \text{ versus } w_o h_o / (w_o + nh_o) * (1 - \sigma_{appl} / \sigma_{ult}) / T^{1/4}$$

Plot should be linear with intercept = 0

x = depth of attack  
 T = temperature, K  
 t = time

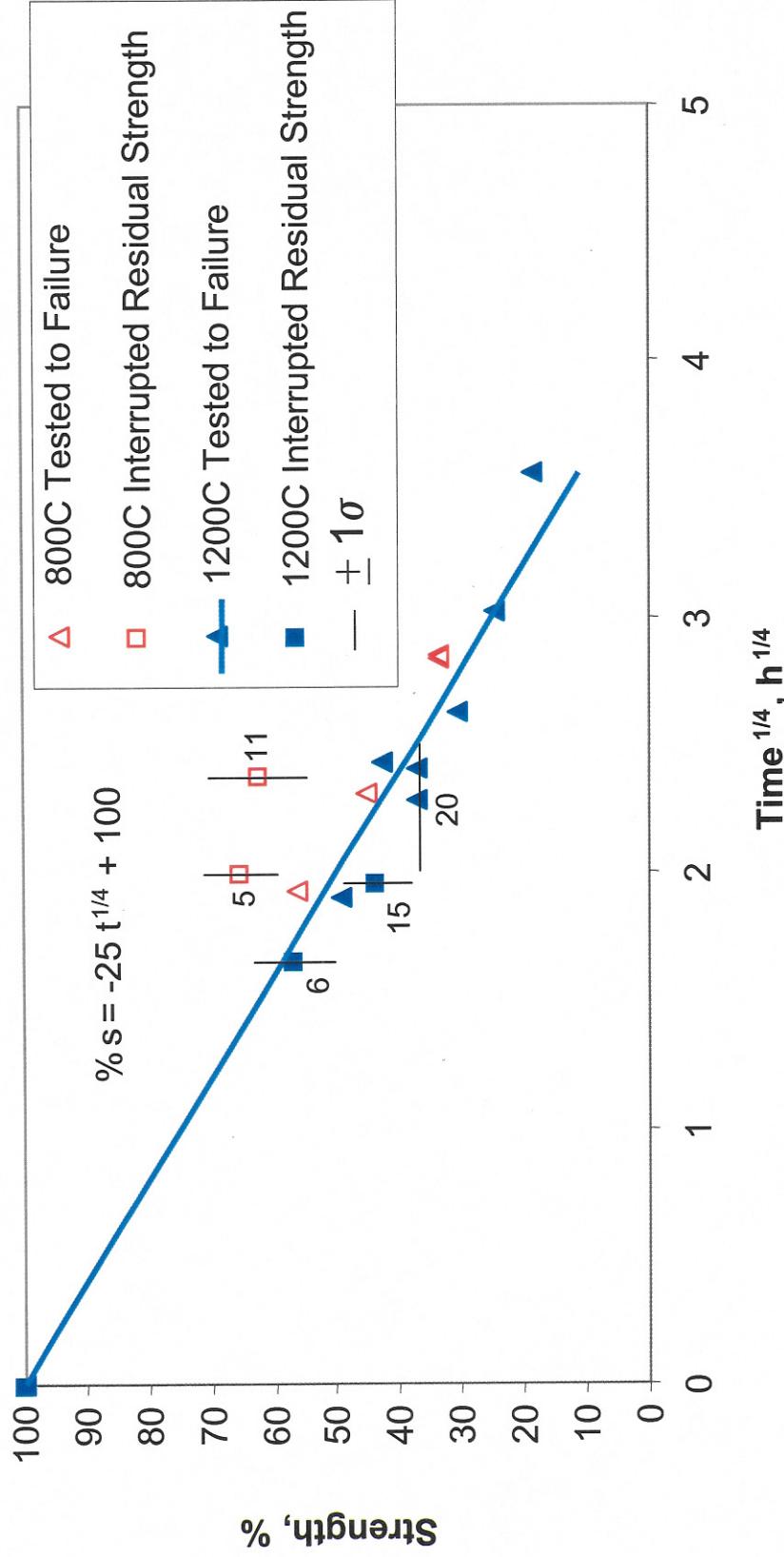
Φ = oxygen mole fraction  
 k<sub>p</sub>, k<sup>\*</sup><sub>p</sub> = parabolic rate constants  
 w<sub>o</sub> = initial specimen width  
 h<sub>o</sub> = initial specimen thickness

## Edge Damage Fits a Parabolic Oxidation Model



- ◆ Normalization = dimension parameter \*  $(1/T^{1/4}) * (1-\sigma_{\text{appl}}/\sigma_{\text{ult}})$ .
- ◆ Agreement with parabolic oxidation model if all data points fall on the same line with y intercept = 0.
- ◆ Data can also be fit to  $t^{1/4}$  time dependence (a better fit).

# Power Law Behavior for Stress Rupture Strength and Residual Strength

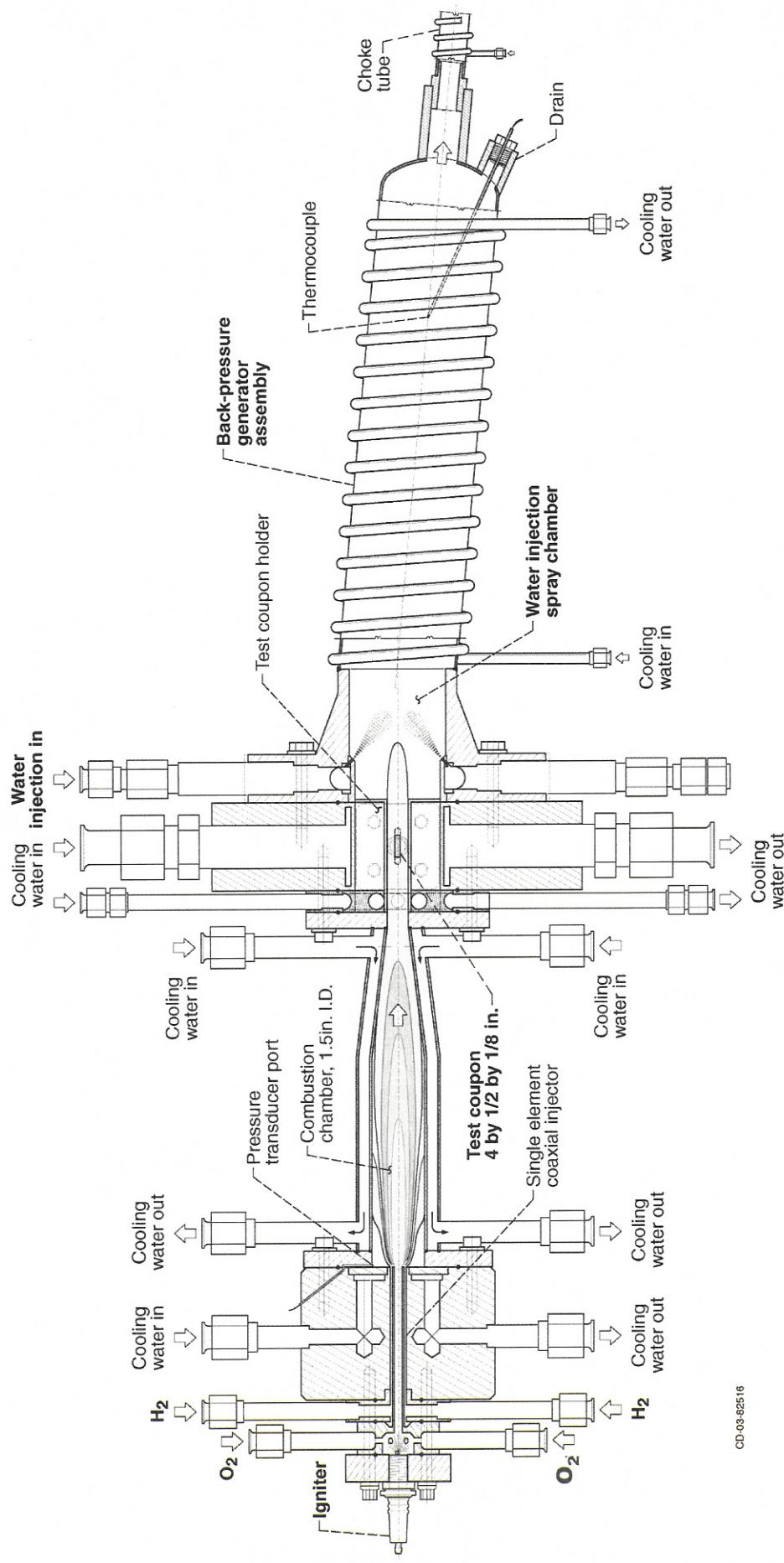


**Exponent of 0.25 fits stress rupture and residual strength loss data**

## Status of Steam Environment Model

- ♦ Objective: Determine SiC recession rate as a function of P, T, gas velocity, gas chemistry
  - 3 O/F's between 1 and 2
  - 3 pressures: 100, 500, 1000 psi
  - Thin film thermocoupled samples
  - Gas velocity ~ 180 m/s (600 ft/s)
  - Weight, recession measured at intervals for a total exposure time of up to 1 hour at each condition.
- ♦ FY'03: Studied recession of SiC coated C/SiC under simulated rocket engine environments.
- ♦ FY'04:
  - Complete recession study
  - Compare results to SiC recession model predictions developed for aircraft engine applications

# Subsonic High-pressure Coupon Test Configuration Used for Determination Of SiC Recess Due to Moisture Generated by Combustion of H<sub>2</sub> and O<sub>2</sub>



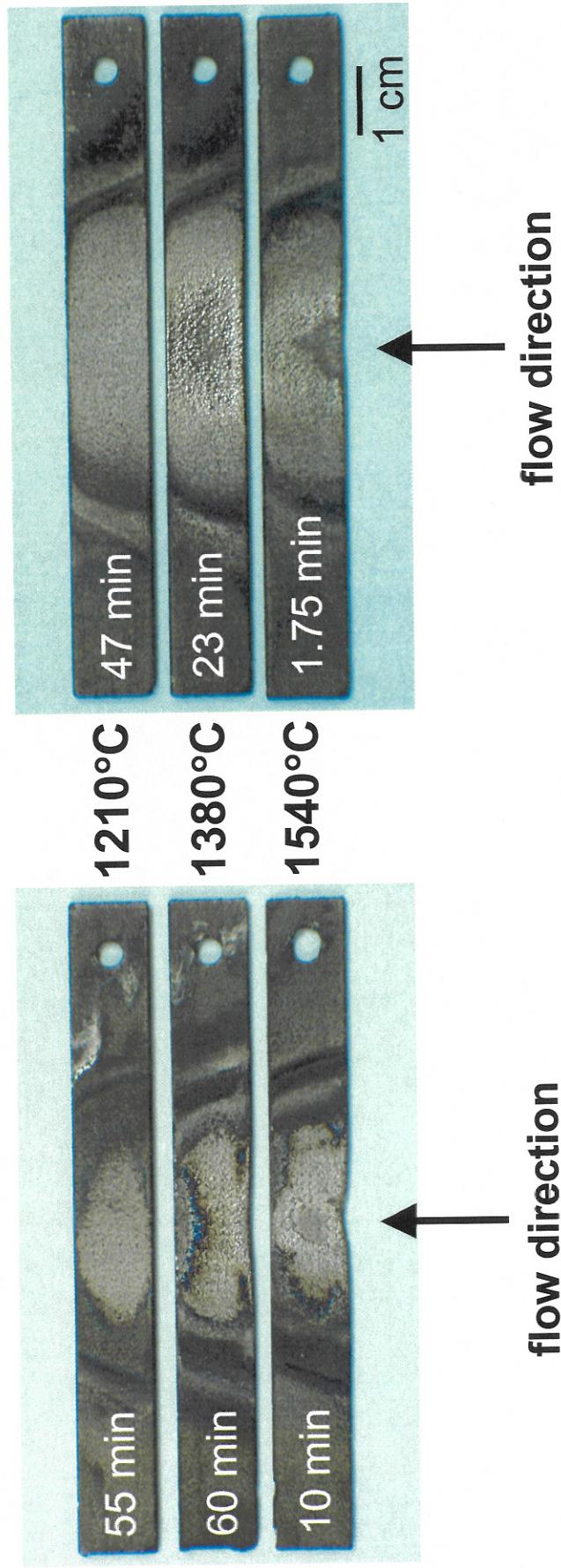
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## SiC Coated C/SiC After Exposure to H<sub>2</sub> / O<sub>2</sub> Combustion

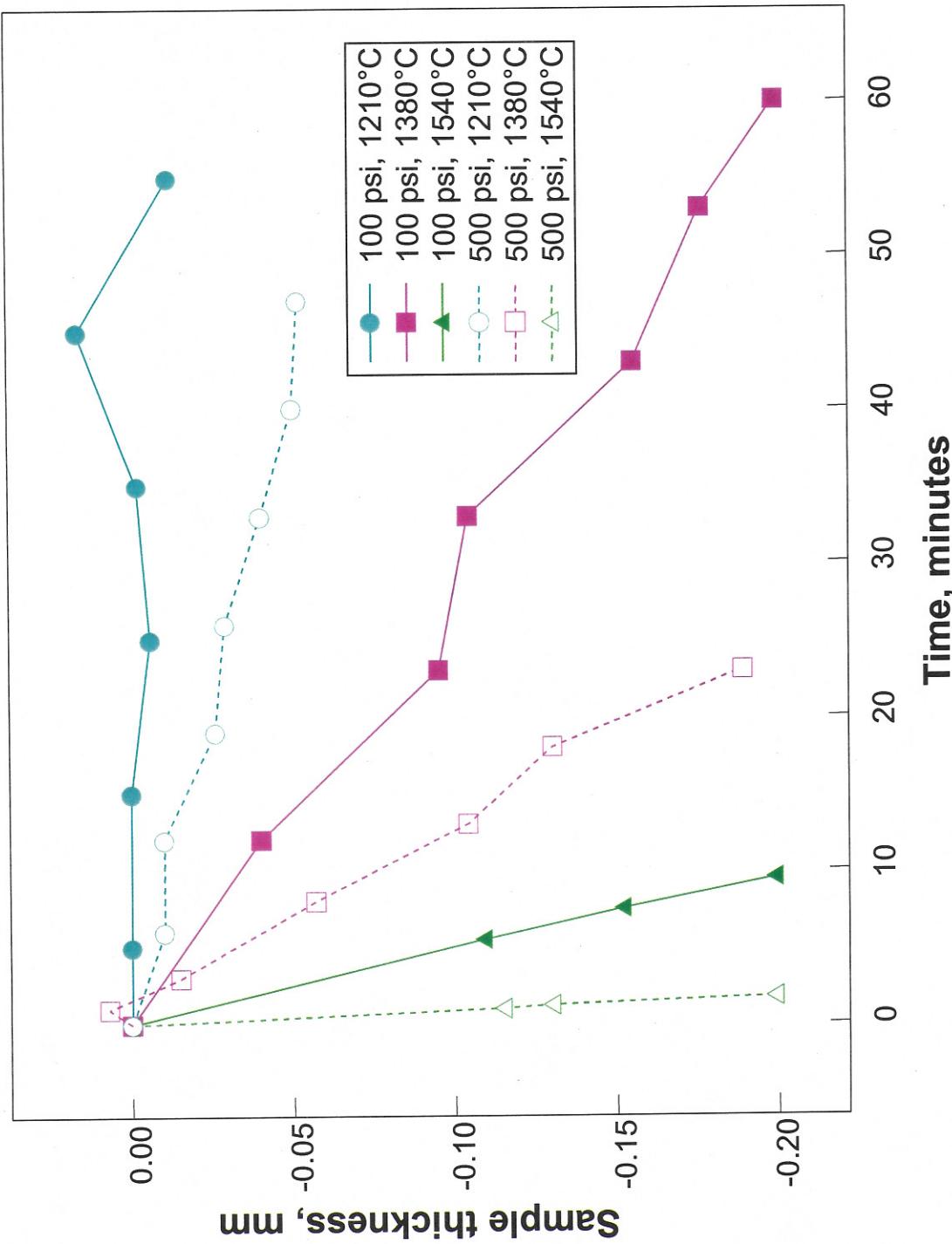
0.625 mm (25 mil) thick SiC seal coat

Total pressure: 6.8 atm

100 psi      Gas velocity: ~ 180 m/sec      500 psi



# SiC Coated C/SiC Recession Measured As Thickness at Leading Edge After Specimen Exposure to Products of H<sub>2</sub> / O<sub>2</sub> Combustion



# Concluding Remarks

- ◆ Fiber oxidation dominates C/SiC behavior. Stress and differential thermal expansion make fibers accessible.
- ◆ Edge effects diminish as specimen width increases.
- ◆ Oxidation based models, with some empiricism, provide a reasonable method for residual strength and life data correlation and prediction over a wide range of pressure, temperature, and applied stress.
- ◆ Much more effort will be required to develop a purely physics based life prediction model, and the physics will be unique to each set of fiber coating, matrix, and external coating constituents.
- ◆ Water vapor strips protective silica scale rapidly at high temperature and water vapor partial pressure. Environmental barrier coating is required.

# Acknowledgements

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The authors thank

- ◆ NGLT Propulsion Research and Technology Project  
for sponsoring this work
- ◆ John Zima for conducting the mechanical tests
- ◆ Drs. John R. Ellis and James A. DiCarlo for their  
many helpful comments during the life of this effort